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Publication date:
2017

Document Version
Peer reviewed version

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Introduction

Lignin is the most abundant aromatic compound on Earth. Lignin is mostly burned as a low quality fuel in pulp mills and biorefineries. Lignosulfonate is a byproduct from sulfite pulping, mainly produced by the company Borregaard [1]. Extraction of higher value products from lignosulfonate is of interest, which is rarely addressed in literature. Amongst different methods, solvothermal conversion assisted by a heterogeneous catalyst is a promising method for conversion of lignin. However, the sulfur in the structure of lignosulfonate deactivates most of the heterogeneous catalysts by sulfur deposition. Conversion of lignosulfonate to liquefied products using sulfur tolerant hydrotreating catalysts is investigated in this work.

Materials and Methods

Spruce based sodium lignosulfonate (Na-LS, Mw= 6700) and ammonium lignosulfonate (NH_4-LS, Mw= 46500), provided by Borregaard, were used as lignin source. Na-LS is further ion-exchanged to proton-lignosulfonate (H-LS). The sulfur content of Na-LS and NH_4-LS are 2.7 and 7 wt%, respectively. Non-catalytic and catalytic experiments with a commercial alumina supported NiMo catalyst (provided by Haldor Topsøe A/S) were conducted at 260-315 ˚C in a 300 ml Parr 4560 batch reactor with ethanol as the reaction medium. Ethanol was chosen since it has been shown to inhibit repolymerization of the in situ degraded lignin compounds and may act as a hydrogen donor [2]. In each experiment, lignin, catalyst (in catalytic tests) and solvent were placed in the reactor, followed by sealing, flushing the reactor with nitrogen and further loading with hydrogen (25 barg). The NiMo catalyst was mostly used directly in its oxide form, assuming that the sulfur in the lignosulfonate may lead to formation of the sulfide form ($NiMoS_2$). However, a few experiments were conducted with a presulfided catalyst in order to address the role of presulfidation on conversion of lignosulfonate. Presulfidation was conducted overnight by treating the catalyst with 10 ml dimethyl disulfide (DMDS) in the batch reactor at 350 ˚C and 30 barg hydrogen pressure. At the end of each experiment, solid and liquid products of the reactions were separated by filtration. Furthermore, the liquid phase was subjected to vacuum evaporation at 35 ˚C and 5 mbar, to isolate light and heavy liquid fractions. The heavy liquid phase remaining unevaporated was regarded as bio-oil. Gas Chromatography-Mass Spectrometry (GC-MS) was used for identification of the compounds in light and oil fractions. The molecular weight distribution of the oil phase was determined by size exclusion chromatography (SEC). Gaseous products were analyzed by GC. Elemental analysis (Eurovector EuroEA3000) was used for quantification of organic C, H, N, S and O content of the oil fraction.

Results and Discussion

The results of the conversion of lignosulfonate on NiMo catalyst are presented in Table 1. The oil yields are calculated based on the dry and ash free lignin. The results show that the oil yield increased by addition of catalyst; the yield of bio-oil from conversion of H-LS at 260 ˚C doubled from 13 to 27 wt%. Increased lignin depolymerization was observed in both non-catalytic and catalytic experiments with increasing temperature: Considering conversion of lignosulfonate at 315 ˚C, an oil yield of 24 wt% was observed in non-catalytic test, while an oil yield of 62 wt% was obtained by introducing the catalyst. The higher oil yields over NiMo catalyst compared to non-catalytic tests might be due to the suppression of repolymerization reactions involving reactive in situ degraded compounds over catalytic active sites. Methyl substituted phenols constitute the main identified compounds in the oil from H-LS conversion on NiMo catalyst at 315 ˚C. The carbon/oxygen (C/O) content of H-LS is 1.9. According to the elemental analysis of the oil fraction from conversion of H-LS at 315 ˚C over NiMo catalyst, the C/O ratio doubled to 4.0, which confirms deoxygenation activity of the catalyst.

Table 1 Results of the catalytic experiments with NiMo. Catalyst: lignin: solvent ratio of 1 g: 10 g: 100 ml at 25 barg initial H_2 pressure and 3 h reaction time

Lignosulfonate	Catalyst	T [˚C]	Oil yield wt%
H-LS	Non-catalytic	260	13
H-LS	Non-catalytic	315	24
H-LS	NiMo (Non-presulfided)	260	27
H-LS	NiMo (Non-presulfided)	315	62
NH_4-LS	NiMo (Non-presulfided)	260	21
NH_4-LS	NiMo (Presulfided)	260	20
NH_4-LS	NiMo (Non-presulfided)	315	34
NH_4-LS	NiMo (Presulfided)	315	37

No significant effect is observed by presulfidation of catalyst for conversion of NH_4-LS: 21 and 20 wt% oil is obtained by conversion of NH_4-LS at 260 ˚C over non-presulfided and presulfided NiMo catalysts. The oil yield from conversion of NH_4-LS at 315 ˚C increased slightly from 34 wt% over non-presulfided catalyst to 37 wt% over sulfided catalyst. Therefore, it can be speculated that presulfidation of NiMo for conversion of lignosulfonate may not be required, presumably due to the successful activation of catalyst by the sulfur content of lignosulfonate. Work is ongoing to verify this hypothesis.

Significance

Good catalytic activity of NiMo catalyst for conversion of sulfonated lignin to liquid products is presented in this work, which may assist the introduction of novel uses of lignin.

References

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